Evaluation of Carbon Nanotubes Functionalized Polydimethylsiloxane Based Coatings for In-Tube Solid Phase Microextraction Coupled to Capillary Liquid Chromatography

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Academic Editor: Mary Boyce

Received: 30 March 2015 / Accepted: 31 July 2015 / Published: 10 August 2015

Abstract: In the present work, the performance of carbon nanotubes (c-CNTs) functionalized polydimethylsiloxane (PDMS) based coatings as extractive phases for in-tube solid phase microextraction (IT-SPME) coupled to Capillary LC (CapLC) has been evaluated. Carboxylic-single walled carbon nanotubes (c-SWNTs) and carboxylic-multi walled carbon nanotubes (c-MWNTs) have been immobilized on the activated surface of PDMS capillary columns. The effect of different percentages of diphenyl groups in the PDMS extractive phase has also been evaluated. The extraction capability of the capillary columns has been tested for different organic pollutants, nitrogen heterocyclic compounds and polycyclic aromatic compounds (PAHs). The results indicated that the use of the c-CNTs-PDMS capillary columns improve pyriproxyfen and mainly PAH extraction. Triazines were better extracted by unmodified TRB-35 and modified c-CNTs-PDMS TRB-5. The results showed that the extraction capability of the c-CNT capillary columns depends not only on the polarity of the analytes (as it occurs with PDMS columns) but also on the interactions that the analytes can establish with the immobilized c-CNTs on the PDMS columns. The extraction efficiency has been evaluated on the basis of the preconcentration rate that can be achieved, and, in this sense, the best c-CNTs-PDMS capillary column for each group of compounds can be proposed.
Keywords: in-tube solid phase microextraction; carbon nanotubes; polydimethylsiloxane; nitrogen heterocyclic compounds and polycyclic aromatic hydrocarbon

1. Introduction

Solid phase microextraction (SPME) is a reliable technique for sample pretreatment owing to its simplicity, rapidity and wide application. SPME integrates sampling, concentration and sample injection in one single step [1]. Moreover, it is a solvent free extraction [2]. These characteristics are especially useful to develop green analytical methodologies [3]. Among the different modalities of SPME, in-tube solid phase microextraction (IT-SPME) provides additional advantages, simplifying the automatization and facilitating on-line coupling to the separation/detection system [4,5]. IT-SPME is based on the extraction of analytes on the coating of a capillary column that is on-line coupled with a liquid chromatographic system [6,7]. Preconcentration can be carried out until equilibrium or until sufficient extraction level is reached.

The nature of the capillary coating for the IT-SPME is a key point to reach satisfactory extraction efficiencies, since the sorption/desorption processes strongly depend on the affinity of the analytes for the coating. Commercially available capillaries have been proposed to determine several analytes for environmental, biological or food applications. However, the utility of conventional coatings is limited mainly by the low extraction efficiencies. Thus, recent research has afforded a variety of alternative capillary coatings to improve extraction efficiency, selectivity, extraction time and coating stability [8–11].

In this scenario, carbon nanotubes (CNTs) [12] opened a new investigation area in the development of alternative coating materials for IT-SPME, since their special properties make them very attractive to improve the performance of this technique. Besides the extraordinary electrical, thermal and mechanical properties, CNTs possess a large surface area. Their strong adsorption affinity to a wide variety of organic compounds, together with their large adsorption surface make them excellent material for (micro)extraction [13,14].

An interesting feature of CNTs is that their surfaces can be chemically modified, resulting in functionalized adsorbents that allow the introduction of new interactions with organic molecules [15]. Modifying the structure of the CNTs, either by covalent or non-covalent functionalization, changes the CNTs’ properties, such as CNT hydrophobicity, or introduces specific substituents which modify the affinity of these adsorbents for the analytes [14].

There are a vast number of publications describing the advantages of using CNTs as adsorbent materials for SPME [16–19]. Moreover, several review articles can be found dealing with this subject [20–22]. However, the use of CNTs or carbon based nanoadsorbents for IT-SPME is still a challenge. Only a few examples of CNTs functionalized capillary columns for IT-SPME can be found [23,24].

The objective of the present work was to evaluate the performance of carboxylic SWNTs-PDMS (c-SWNTs-PDMS) and carboxylic MWNTs-PDMS (c-MWNTs-PDMS) coatings as extractive phases for IT-SPME coupled to Cap-LC. The extraction efficiency, precision and sensitivity for nitrogen heterocyclic compounds and polycyclic aromatic hydrocarbons PAH [25] compounds compared with the extraction efficiency of commercial PDMS capillary columns has been studied in order to elucidate the potential advantage of using c-CNTs-PDMS as the extractive phase for IT-SPME.
2. Experimental Section

2.1. Chemicals

SWNTs, MWNTs, 3-aminopropyl trithoxysilane (APTS), 1,3-dicyclohexylcarbodiimide, glutaraldehyde, and the triazines (atrazine, propazine, terbuthylazine-desethyl (DES-TBA) and terbuthylazine-2-hydroxy (2-OH-TBA) were purchased from Sigma-Aldrich (Germany). Pyriproxyfen were obtained from Sigma (St, Louis, MO, USA). Terbuthylazine (TBA) and PAH-Mix 18 (acenaphthene acenaphthylene, anthracene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3,c,d]pyrene, naphthalene, phenanthrene, perylene and pyrene) were supplied by Dr Ehrenstorfer (Germany). Acetonitrile was of HPLC grade (Scharlau, Barcelona Spain). The ultrapure water was obtained through a system Nanopure II (Sybron, Barnstead, United Kingdom).

2.2. Equipment

The capillary chromatographic system consisted of a capillary LC binary gradient pump (Agilent 1200 Series, Waldbronn, Germany), a six-port injection valve (Rheodyne 7725) and a UV-Vis diode array detector (HP 1200 series) equipped with an 80 nL flow cell. The analytical signal was recorded between 210 and 360 nm. A Zorbax SB C18 (150 mm × 0.2 mm i. d., 0.5 µm) particulate column (Agilent) was employed for analyte separation.

The c-CNTs were characterized using FTIR-ATR Agilent Technologies Cary 630 FTIR (Agilent, USA). The micrographs of scanning electronic microscope (SEM) were obtained with a HITACHI-S4800 operating at 20 kV.

2.3. Functionalization of the Capillary Columns

SWNTs and MWNTs were carboxylated prior to their immobilization on the capillary column inner surface. Figure 1 shows the structure of the CNTs used in this work. Carboxylation of CNTs was carried out following the procedures described in [26,27] for SWNTs and MWNTs, respectively. Briefly, to prepare c-SWNTs, 5 mL of H2SO4:HNO3 (3:1) were added to 0.025 g of SWNTs and ultrasonicated for 90 min (50 W, 60 Hz). Then, this mixture was diluted with water (500 mL) and filtered through a 0.45 μm cellulose acetate filter. Finally, c-SWNTs were washed with 1 M HCl and left to dry at room temperature. The c-MWNTs were prepared by adding 80 mL of H2SO4:HNO3 (3:1) to 0.020 g of MWNTs, and ultrasonicated for 5 h. Next, the suspension was diluted with water (1.5 L), filtered and washed with water [22].

The following step was the c-CNT immobilization on the inner surface of the PDMS capillary columns (see Figure 1). Firstly, activation of the PDMS capillary column was carried out. For this purpose, the column was rinsed with a NaOH solution (2 M) and left to act for 24 h [28]. Next, ultrapure water was passed through the capillary column (5 min) followed by 2% (v/v) APTS prepared in anhydrous acetone (15 min), water (5 min) and methanol (5 min) to eliminated the excess of APTS. In the next step, 10% (v/v) glutaraldehyde dissolved in 50 mM borate buffer at pH 9.0 was passed through the capillary for 10 min. Then, c-CNTs (5 mg/mL) dispersed in 4.5 mL of dimethylformamide containing 0.5 mg of 1,3-dicyclohexylcarbodiimide were passed through the capillary for 30 min. Finally the capillary was rinsed with water to remove the unreacted c-CNTs.
Figure 1. (A) Equivalent phase of a PDMS\textsubscript{TRB-5} and PDMS\textsubscript{TRB-35} capillary columns coating, (B) SWNTs, diameter = 0.7–104 nm and (C) MWNTs, diameter = 7–15 nm.

2.4. IT-SPME Procedure and Chromatographic Conditions

The injection loop of an injection valve was replaced by a 40-cm segment of a GC capillary column of PDMS functionalized with c-SWNTs and c-MWNTs. The PDMS capillary columns used in this work were TRB-35 (35% diphenyl and 65% dimethyl polysiloxane) and TRB-5 (5% diphenyl and 95% dimethyl polysiloxane) (0.32 mm i. d. y 3.0 μm thickness). Capillary connections to the valve were facilitated by the use of 2.5 cm sleeve of 1/16 in polyether ether ketone (PEEK) tubing; 1/16 in PEEK nuts and ferrules were used to complete the connections. The schematic diagram of the IT-SPME system is shown in Figure 2. Aliquots of 4 mL of standard solutions of triazines (50 μg/L), and pyriproxyfen (50 μg/L) and 2 mL of PAHs (up to 100 μg/L) were manually loaded into the system by means of 1.0 mL precision syringe. A clean-up step was also carried out by injecting 50 μL of ultrapure water after the sample loading. The injection of the retained analytes was performed by rotating the valve to the inject position.

Figure 2. Schematic diagram of IT-SPME-Cap-LC- diode array detector DAD system.
The analysis of triazines was carried out in isocratic elution mode using acetonitrile: water (70:30). Gradient elution mode was used for the chromatographic separation of PAHs: the percentage of acetonitrile was increased from 70% at zero min to 90% at 10 min, then to 100% at 24 min; and decreased to 70% at 27 min. Pyriproxyfen were also analyzed in gradient elution mode with acetonitrile/water, in this case, the initial percentage of acetonitrile was 70%; this percentage was increased to 100% at 8 min, remained constant until 18 min, and then decreased to 70% at 20 min. In all the cases the flow rate was 10 μL/min. Acetonitrile and water were filtered through 0.45 μm nylon membrane before use.

3. Results and Discussion

3.1. Characterization of c-CNTs and Capillary Columns

Characterization of c-CNTs after the carboxylation process was carried out by ATR-FTIR. Figure 3 shows the IR spectra obtained for c-SWNTs and c-MWNTs. Besides the CH₂ band at 1360 cm⁻¹, absorption bands at 1120 and 1710 cm⁻¹ were in correspondence with C–O and C=O stretching, respectively, corroborating the existence of carboxyl groups in the functionalized SWNTs and MWNTs [26,27].

Figure 3c,d depict the SEM micrographs of the inner surface of c-SWNTs-PDMS_TRB-5 and c-MWNTs-PDMS_TRB-5 capillary columns, showing the resulting coating on the surface of the capillary column. It should be remarked, that the coatings were homogeneous all along the capillary columns. A similar coating was observed in the case of c-CNTs-PDMS_TRB-35 capillary columns (micrographs not shown).

Figure 3. IR spectra of (a) c-SWNTs, (b) c-MWNTs, and SEM micrographs of (c) c-SWNTs-PDMS_TRB-5 and (d) c-MWNTs-PDMS_TRB-5.
3.2. Study of the Extraction Capability of the c-CNTs-PDMS Coated Capillary Columns for Nitrogen Heterocyclic Compounds

The target analytes were 2-OH-TBA, DES-TBA, propazine, atrazine, TBA and pyriproxyfen. 4 mL of a mixture of triazines (50 µg/L) and pyriproxyfen (10 µg/L) were processed in the IT-SPME-Cap-LC system. Figure 4 shows the analytical responses obtained for triazines with the different capillary columns at the above mentioned concentration level. The structures of the analytes are given in Table 1.

![Figure 4](image_url)

**Figure 4.** Analytical response of nitrogen heterocyclic compounds (50 µg/L) obtained with PDMS and c-CNTs-PDMS coated capillary columns and employed to perform IT-SPME. Error bars represent standard deviation for n = 3.

Figure 4 shows that the use of commercial PDMS TRB-35 capillary columns for triazines extraction was advantageous compared with the use of PDMS TRB-5. PDMS TRB-5 coating contains a 5% phenyl groups that provides a characteristic affinity towards aromatic rings while the percentage of phenyl groups in the PDMS TRB-35 coating is higher, which increases the polarity of the capillary column. Therefore, the extraction of triazines was favored when the PDMS TRB-35 capillary column was used. In the case of pyriproxyfen, the extraction efficiency was slightly better with the PDMS TRB-5 capillary column. The extraction efficiency determines the analyte responses. However, the limits of detection (LODs) are determined by other factors, mainly the features of the baseline in the region where the analytes eluted. Therefore, the LODs were experimentally established as concentrations that produced a peak with a signal to noise ratio of 3. Table 1 summarizes the LODs under the experimental conditions described in Section 2. C-SWNTs-PDMS TRB-5 capillary column provided better LODs values for atrazine and terbuthylazine, similar to those achieved with the PDMS TRB-35 capillary column.
Table 1. Structure of target analytes and limit of detection (LOD) achieved with different capillary columns using the synthesized capillary columns.

<table>
<thead>
<tr>
<th>NAME</th>
<th>STRUCTURE</th>
<th>L.O.D. (µg/L)</th>
<th>PDMS&lt;sub&gt;TRB-35&lt;/sub&gt;</th>
<th>c-SWNTs-PDMS&lt;sub&gt;TRB-35&lt;/sub&gt;</th>
<th>c-MWNTs-PDMS&lt;sub&gt;TRB-35&lt;/sub&gt;</th>
<th>PDMS&lt;sub&gt;TRB-5&lt;/sub&gt;</th>
<th>c-SWNTs-PDMS&lt;sub&gt;TRB-5&lt;/sub&gt;</th>
<th>c-MWNTs-PDMS&lt;sub&gt;TRB-5&lt;/sub&gt;</th>
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<tr>
<td>Terbuthylazine-2-hydroxy (2-OH-TBA)</td>
<td><img src="image" alt="Structure" /></td>
<td>3.5</td>
<td>16</td>
<td>14</td>
<td>5</td>
<td>7</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Terbuthylazine-desethyl (DES-TBA)</td>
<td><img src="image" alt="Structure" /></td>
<td>4</td>
<td>6</td>
<td>7</td>
<td>4</td>
<td>7</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Atrazine</td>
<td><img src="image" alt="Structure" /></td>
<td>1.2</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>1.3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Propazine</td>
<td><img src="image" alt="Structure" /></td>
<td>0.7</td>
<td>1.9</td>
<td>5</td>
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<td>1.1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Terbuthylazine (TBA)</td>
<td><img src="image" alt="Structure" /></td>
<td>0.4</td>
<td>0.8</td>
<td>1.3</td>
<td>0.5</td>
<td>0.4</td>
<td>0.6</td>
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<tr>
<td>Pyriproxyfen</td>
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<td>0.1</td>
<td>0.06</td>
<td>0.05</td>
<td>0.08</td>
<td>0.08</td>
<td>0.07</td>
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Table 1. Cont.

<table>
<thead>
<tr>
<th>NAME</th>
<th>STRUCTURE</th>
<th>L.O.D. (µg/L)</th>
<th></th>
<th></th>
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<td></td>
<td></td>
<td>PDMST&lt;sub&gt;RB-35&lt;/sub&gt;</td>
<td>c-SWNTs&lt;sub&gt;-PDMSTRB-35&lt;/sub&gt;</td>
<td>c-MWNTs&lt;sub&gt;-PDMSTRB-35&lt;/sub&gt;</td>
<td>PDMSTRB&lt;sub&gt;-5&lt;/sub&gt;</td>
<td>c-SWNTs&lt;sub&gt;-PDMSTRB-5&lt;/sub&gt;</td>
<td>c-MWNTs&lt;sub&gt;-PDMSTRB-5&lt;/sub&gt;</td>
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<tr>
<td>Naphtalene</td>
<td><img src="image" alt="Naphtalene" /></td>
<td>0.15</td>
<td>0.23</td>
<td>0.33</td>
<td>0.23</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td><img src="image" alt="Benzo[b]fluoranthene" /></td>
<td>0.35</td>
<td>0.37</td>
<td>0.21</td>
<td>0.17</td>
<td><strong>0.03</strong></td>
<td>0.07</td>
</tr>
<tr>
<td>Dibenzo[a,h]anthracene</td>
<td><img src="image" alt="Dibenzo[a,h]anthracene" /></td>
<td>3.85</td>
<td>0.33</td>
<td>0.83</td>
<td>0.88</td>
<td><strong>0.14</strong></td>
<td>0.29</td>
</tr>
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</table>
The results obtained with the c-SWNTs or c-MWNTs-PDMS coatings must be addressed considering the affinity of the PDMS capillary towards triazines but also the interactions that the c-CNTs-PDMS based capillary coatings can establish with the triazines. CNTs can interact with triazines through π-π interactions, however in this work c-CNTs have been used and then, ion exchange interactions and hydrogen bonds could also be involved [23]. Experimentally, it was observed that the presence of c-CNTs in the PDMSTRB-35 capillary column resulted in a decrease of the analytical response for triazines, and so an increase of their LODs (see Figure 4 and Table 1). However, the pattern for both PDMSTRB-5 and c-CNTs-PDMSTRB-5 was different. Similar or better results were obtained for atrazine, propazine and terbutylazine with the c-SWNTs-PDMSTRB-5 capillary column than those achieved with PDMSTRB-5 capillary column. This slight improvement on the extraction could be explained considering π-π interactions, since hydrogen bonds and ion exchange would provide a more significant increase on the extraction efficiency. As mentioned above, similar results were obtained with PDMSTRB-35 and c-SWNTs-PDMSTRB-5 for trade triazines. In the case of pyriproxyfen, Table 1 shows that the c-MWNTs-PDMSTRB-35 capillary coating was the best option since the LOD was lower compared with the other studied capillary coatings. Probably, this enhancement was also due to the π-π interactions between the aromatic systems of the analyte and the c-CNTs immobilized on the surface of the capillary column [29].

3.3. Study of the Extraction Capability of the c-CNTs-PDMS Capillary Columns for PAHs

PAHs include a number of hydrocarbons compounds with different polarity [30]. Naphthalene, benzo[b]fluoranthene and dibenzo[a,h]anthracene were chosen as target analytes (100 µg/L). Noted that the retention times at the experimental chromatographic conditions were \( t_r = 5.2 \) min, \( t_r = 13.5 \) min and \( t_r = 23 \) min for naphthalene, benzo[b]fluoranthene and dibenzo[a,h]anthracene, respectively. As expected, the use of the commercial PDMSTRB-5 capillary column provided better results than the PDMSTRB-35 column for the more apolar PAHs, while the PDMSTRB-35 capillary was more adequate for the more polar PAHs (Figure 5 and Table 1). These results can be explained by the lower polarity of the PDMSTRB-35 compared with the PDMSTRB-35 capillary.

The presence of c-CNTs on the surface of the PDMS capillary columns gave rise to differences on the interactions of the capillary coating towards the analytes that resulted in differences to the analytical response, and so on with the LODs. As can be seen in Figure 5, the extraction efficiency of the PDMS columns for PAH compounds was strongly enhanced by the presence of c-CNTs in the case of TRB-5, particularly when c-SWNTs were immobilized on these capillaries. This improvement can be explained by the π-π interactions between the aromatic rings of the PAHs and the c-CNTs.

3.4. Precision

Precision was evaluated for all the analytes at concentration level of 50 µg/L for triazines and pyriproxyfen and 100 µg/L for PAHs. Relative standard deviations (%RSD) obtained with the different capillary coatings are shown in Table 2. As can be seen, run-to-run %RSD values were lower than 9%. These results indicated that satisfactory %RSD values were achieved with all the capillary columns studied. Capillary-to-capillary precision was also evaluated. For this aim, we compared the extraction efficiency obtained for a mixture of the triazines (50 µg/L) or PAHs (100 µg/L) with two c-CNTs-PDMS capillaries columns prepared under identical conditions. Capillary-to-capillary %RSD values were lower
than 19% for all the analytes. The low RSD values bear evidence to the fact that the use of c-CNTs-PDMS capillary columns was a reliable and reproducible approach to be employed for IT-SPME extraction.

![Graph](image1.png)

**Figure 5.** Analytical response of PAHs with PDMS and c-CNTs-PDMS capillary columns used for IT-SPME. Error bars represent the standard deviation for n=3.

**Table 2.** Run-to run relative standard deviation (%RSD) calculated for triazines (50 µg/L) and PAHs (100 µg/L).

<table>
<thead>
<tr>
<th>RSD (%)</th>
<th>PDMS&lt;sub&gt;TRB 5&lt;/sub&gt;</th>
<th>c-SWNTs-PDMS&lt;sub&gt;TRB 5&lt;/sub&gt;</th>
<th>c-MWNTs-PDMS&lt;sub&gt;TRB 5&lt;/sub&gt;</th>
<th>PDMS&lt;sub&gt;TRB 35&lt;/sub&gt;</th>
<th>c-SWNTs-PDMS&lt;sub&gt;TRB 35&lt;/sub&gt;</th>
<th>c-MWNTs-PDMS&lt;sub&gt;TRB 35&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-OH-TBA</td>
<td>1.2</td>
<td>1.8</td>
<td>2</td>
<td>4.3</td>
<td>1.2</td>
<td>6.1</td>
</tr>
<tr>
<td>DES-TBA</td>
<td>1.9</td>
<td>1.2</td>
<td>6.5</td>
<td>5.2</td>
<td>4.1</td>
<td>3.8</td>
</tr>
<tr>
<td>Atrazine</td>
<td>3.8</td>
<td>3.8</td>
<td>7.7</td>
<td>7.3</td>
<td>6.0</td>
<td>6.9</td>
</tr>
<tr>
<td>Propazine</td>
<td>2.3</td>
<td>3.9</td>
<td>1.1</td>
<td>3.4</td>
<td>2.2</td>
<td>2.1</td>
</tr>
<tr>
<td>TBA</td>
<td>1.5</td>
<td>0.9</td>
<td>1.1</td>
<td>1.6</td>
<td>1.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Pyriproxyfen</td>
<td>1.8</td>
<td>1.2</td>
<td>2.2</td>
<td>1.6</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>7.3</td>
<td>5.7</td>
<td>4.9</td>
<td>7.6</td>
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<td>5.1</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>8.5</td>
<td>2.8</td>
<td>7.7</td>
<td>2.7</td>
<td>1.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Dibenz[a,h]anthracene</td>
<td>4.2</td>
<td>6.8</td>
<td>6.3</td>
<td>6.4</td>
<td>8.6</td>
<td>4.7</td>
</tr>
</tbody>
</table>

3.5. Evaluation of the Preconcentration Ration Achieved with the c-CNTs-PDMS Capillary Coatings.

A ratio PR was defined in order to compare the results obtained from all extractive phases:

\[
PR = \frac{PA_{c\text{-CNTs--PDMS}}}{PA_{PDMS}}
\]
where $PA$ is the peak area obtained for the respective capillary column coatings. Table 3 shows the $PR$ values obtained for each analyte with the c-SWNTs-PDMS and c-MWNTs-PDMS capillary columns and considering the unmodified PDMS phases TRB-5 and TRB-35. C-CNTs-PDMS coated capillary columns can introduce interactions, such as $\pi$-$\pi$ stacking, H bonds or ion exchange interactions. However, for the target analytes studied in this work, $\pi$-$\pi$ stacking is the dominant interaction.

The $PR$ values for PAHs were higher than those ratios obtained for the other families of compounds tested, in particular when the c-SWNTs-PDMS TRB-5 was used. Such behavior is attributed to the strong $\pi$-$\pi$ interactions between the aromatic rings of PAHs and the c-CNTs based coating. It should be noted that extraction of PAHs depends on the size of the $\pi$-electron conjugated system of organic molecules that are adsorbed on the surface of CNTs [31]. The c-SWNTs-PDMS TRB-5 capillary column provided the highest analytical response when it was used as the extractive phase for IT-SPME-Cap-LC for PAHs and similar responses for trade triazines than TRB-35 coating. However, pyriproxyfen is better extracted by c-MWNTs-PDMS TRB-35 and c-MWNTs-PDMS TRB-5 capillary columns, respectively.

### Table 3. Preconcentration rate (PR) achieved for the target analytes.

<table>
<thead>
<tr>
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<tr>
<td>2-OH-TBA</td>
<td>1.82</td>
<td>0.6</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
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<tr>
<td>DES-TBA</td>
<td>2.30</td>
<td>0.8</td>
<td>0.4</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>Atrazine</td>
<td>2.61</td>
<td>2.1</td>
<td>1.3</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Propazine</td>
<td>2.93</td>
<td>1.0</td>
<td>1.1</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>TBA</td>
<td>3.21</td>
<td>1.4</td>
<td>0.8</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>3.37</td>
<td>4.0</td>
<td>3.2</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Pyriproxyfen</td>
<td>5.37</td>
<td>1.0</td>
<td>1.1</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>6.04</td>
<td>4.9</td>
<td>2.4</td>
<td>0.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Dibenz[a,h]anthracene</td>
<td>6.86</td>
<td>6.3</td>
<td>3.0</td>
<td>1.2</td>
<td>4.6</td>
</tr>
</tbody>
</table>

### 4. Conclusions

In the present work, the extraction capability of c-CNTs-PDMS coated capillary columns has been evaluated as an alternative for their use in IT-SPME-Cap-LC. C-SWNTs-PDMS and c-MWNTs-PDMS coated capillary columns have been successfully synthetized and their analytical performance has been shown for different compounds such as nitrogen heterocyclic compounds and PAHs. In addition, the percentage of diphenyl groups (5% and 35%) on the PDMS extractive phase has also been considered.

The enhancement of the extraction efficiency of each coating is a function of the affinity of the PDMS coating towards the analytes and the different interactions that can take place between the analytes and the c-CNTs present in the coating material. A significant enhancement of the extraction efficiency of PAHs occurs with the c-CNTs-PDMS capillary columns, and this improvement can be attributed to $\pi$-$\pi$ interactions. The results indicated that this enhancement depends on the presence of biphenyl groups in the PDMS and on the structure of CNTs, c-SWNTs or c-MWNTs. Under the experimental conditions of this work, we have demonstrated that the best extraction for PAHs was achieved with the c-SWNTs-PDMS TRB-5 capillary column. This extractive phase also shows improved results compared with unmodified PDMS TRB-5 for trade triazines. Pyriproxyfen is better extracted by c-MWNTs-PDMS TRB-35.
and c-MWNTs-PDMSTRB-5, respectively. Therefore, the structure of the analytes plays a key role for practical applications of c-CNT based PDMS coatings for IT-SPME coupled to a chromatographic system. However, if all tested compounds want to be screened, the best capillary option is the sorbent c-SWNTs-PDMSTRB-5 achieving a good compromise bearing in mind its extraction efficiency.

Acknowledgments

The authors thank the Ministerio de Economía y Competitividad of Spain (Grant CTQ2014-53916-P) and the Generalitat Valenciana (Grants PROMETEO Program 2012/045) for financial support received.

Author Contributions

The manuscript was written through contributions of all authors and all authors have given approval to the final version.

Conflicts of Interest

The authors declare no conflict of interest.

References


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